

Phosphoric acid rate addition effect in the hydroxyapatite synthesis by neutralization method

Gouveia, D. S., Bressiani, A. H. A., Bressiani, J. C.

Instituto de Pesquisas Energéticas e Nucleares –IPEN – CCTM - Av. Prof. Lineu Prestes,
2242 – 05508-000 - São Paulo-SP, Brasil
E-mail: dsgouvei@ipen.br

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Abstract: Calcium phosphates with different Ca/P molar ratio can be obtained depending the precipitation conditions such as pH and temperature. In this work the effect of the pH's variation during the H₃PO₄ addition in the synthesis of hydroxyapatite-HA, (Ca/P molar ratio 1.67) by neutralization method, was studied. The H₃PO₄ addition's rate was 1.0, 1.5, 8.0 mL.min⁻¹ and in other experiment the H₃PO₄ was added at a time. After the addition was completed the pH ranged from 7-12. The suspensions were kept during 24 hours for ripening. The precipitate was separated from the suspension by vacuum filtration, washed with distilled water and dried at 70°C/24h. Afterwards the materials were analyzed by thermogravimetric analysis (TGA) with heating rate of 10°C/min in air. The calcination of the powders was accomplished at 800°C/3h with heating rate of 10°C.min⁻¹. The powders were characterized by X-ray diffraction (XRD), infrared spectrometry (FTIR), specific surface area (BET), and scanning electron microscopy (SEM). The results indicated that the ratio of addition of the acid can influence both the morphology and the formation of the phases (HA and TCP) in the obtained powders.

Introduction

Hydroxyapatite-HA (Ca₁₀(PO₄)₆(OH)₂), has been widely employed as biomaterial in the form of powders, dense or porous bodies and coatings for metallic or polymeric implants [1, 2]. Its properties such as cristallinity, thermal stability and solubility have been shown to be dependent on the fabrication route [3]. The precipitation reaction by neutralization method had been used and involves the dissolution of calcium hydroxide and electrolysis of the orthophosphate ions [4]. In general, a metaestable phase is formed first and undergoes one or more solution mediated recrystallization steps until the thermodynamically stable modifications precipitates. For low supersaturation the sequence in which each phase is formed is in accordance with the Ostwald rule of stages that allows to predict which compounds will be formed in determined conditions of the process [5,6,7].

Phosphoric acid is a poliprotic acid and its dissociation occurs in three steps given three equivalence points for the chemistry system with pka different (Fig 1) [8]. The protons are donates successively by the poliprotics acid with an acid constant that decrease significantly and give distinct values for each dissociation: $K_{a1} > K_{a2} > K_{a3}$. A simple explanation for this tendency may be attributed to the electrostatic force where the ionization of the second proton of H₃PO₄ involves the removal of one H⁺ of the monovalent anion (H₂PO₄⁻). The removal of third proton is more difficult due to involve the divalent anion removal (HPO₄²⁻) [8].

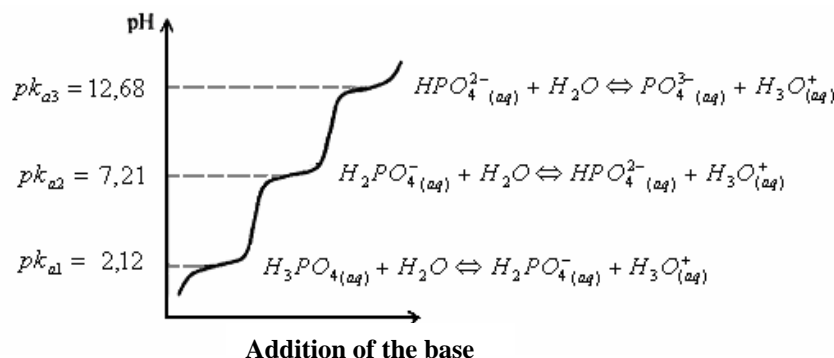


Fig 1 Steps of H_3PO_4 dissociation [8]

However, the neutralization method needs parameters highly qualified and controlled such as the nature and composition of the starting materials, pH control, rate of acid addition and temperature of the solutions prepared to obtain HA monophase. In the present study was evaluated the effect of the pH variation during the H_3PO_4 addition in the synthesis of hydroxyapatite - HA.

Experimental

Synthesis of HA powders was performed based on the neutralization method using 0.3M phosphoric acid and 0.5M calcium hydroxide as precursors. The phosphoric acid solution was added in the calcium hydroxide suspension in the rates: S1 = 1.0; S2 = 1.5; S3 = 8.0 $mL \cdot min^{-1}$ and, in other experiment the H_3PO_4 was added at a time (S4). During the H_3PO_4 addition's, the pH was monitored with a pH meter. After the complete addition, the HA suspensions were kept during 24 hours for ripening. The precipitates were separated from the suspension by vacuum filtration, washed with distilled water and the filtered cakes were placed in an oven kept at $70^\circ C/24h$.

The as-prepared powders were characterized by thermogravimetric analyses (TGA; SHIMADZU 50H) with a heating rate of $10^\circ C \cdot min^{-1}$ in a current of air. The X-ray diffraction (XRD; Rigaku, Multiflex model; $CuK\alpha$) technique was used to identify the phases in the as-prepared and in the calcined powders at $800^\circ C/3h$. The calcined powders at $800^\circ C/3h$ were characterized by infrared spectroscopy (Thermo Nicolet 670 - FTIR – NEXUS; range 3000 to 400 cm^{-1} using KBr pellets). The specific surface area was measured by BET method (Micrometric model ASAP 2000). The powder morphology was assessed by scanning electron microscopy (SEM; Philips-XL 30).

Results and discussion

The pH variation during the phosphoric acid addition in the suspension is showed in the Fig 2. The pH of the reaction can be expected to change due to the dissolution and dissociation of the Ca and PO_4^{3-} precursors. The weakly acid nature of the Ca salts and the highly basic characteristic of the phosphate precursors rendered the reaction instantaneous. All the samples showed a high initial pH (>8.0) where HA is known to be stable [9].

When the addition was performed at $1.0\text{ mL} \cdot min^{-1}$ (S1) the final's pH of the suspension was near 8 and when the rate of addition increased, a more alkaline suspension was achieved with pH near to 11 (S3) (Fig 2). On the other hand, when the phosphoric acid solution was added at a time (S4), the pH was near 5 at first and after a period of 12 min, it reached to 12 remaining for 1 hour (Fig 2). This reduction of pH can be interpreted in terms

of the hydroxyl ions originally present in the $\text{Ca}(\text{OH})_2$ suspension that are readily consumed by the H^+ of the acid phosphoric under a very high addition rate, decreasing pH in the bulk apart from the calcium hydroxide particles far below 12.68 pKa of the reaction [4,10]. After the period determined (≈ 10 min) the reaction was in equilibrium increasing the pH. The H_3PO_4 dissociation for S4 synthesis (Fig 2) occurs in steps and this behavior is confirmed through the phosphoric acid dissociation curve (Fig 1). According to Seckler et al (1999) the slow rate of addition prevents the extreme reduction of pH and the possible substitution of the phosphate group for the hydrogenophosphate (HPO_4^{2-}) [7].

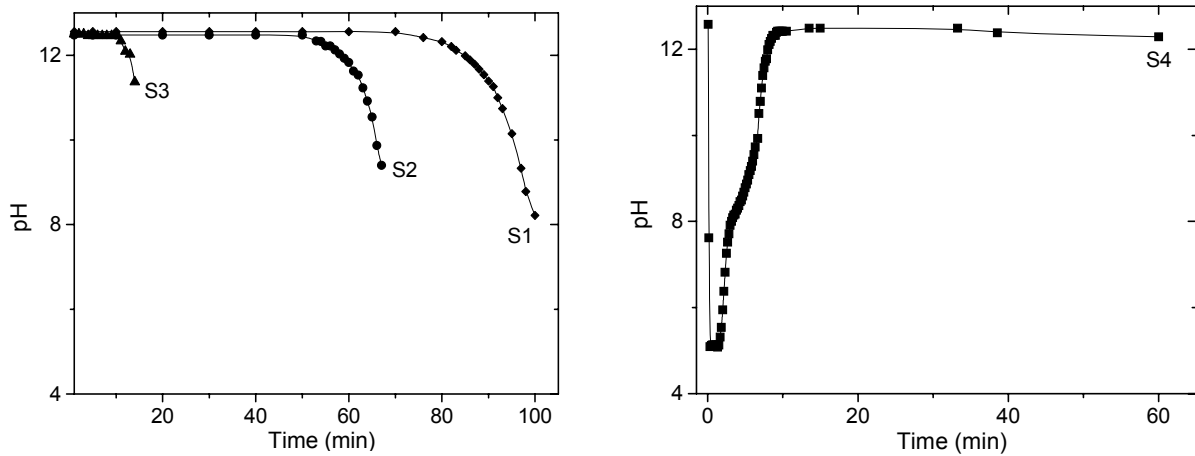


Fig 2. Variation of pH when the H_3PO_4 solution is added. S1 = $1.0 \text{ mL}\cdot\text{min}^{-1}$; S2 = $1.5 \text{ mL}\cdot\text{min}^{-1}$; S3 = $8.0 \text{ mL}\cdot\text{min}^{-1}$ and S4 = fast addition.

Fig 3 shows the thermogravimetric curve of precipitates heated from room temperature to 1000°C . According to the literature, HA has two types of water in its structure – adsorbed and lattice water [11,12]. The results found in this research, demonstrate a significant weight loss up to 400°C for all samples which was probably due to the loss of adsorbed (up to $\approx 200^\circ\text{C}$) and lattice water (up to $\approx 400^\circ\text{C}$). The gradual weight decrease from 400 to 1000°C may be a result of the slow elimination of the carbonate groups linked to HA [9].

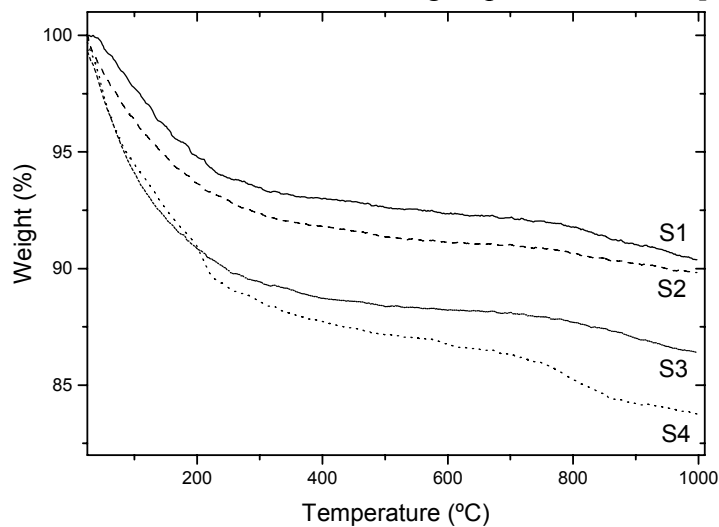


Fig 3 Thermogravimetric curve of precipitates. S1 = $1.0 \text{ mL}\cdot\text{min}^{-1}$; S2 = $1.5 \text{ mL}\cdot\text{min}^{-1}$; S3 = $8.0 \text{ mL}\cdot\text{min}^{-1}$ and S4 = fast addition

The X-ray diffraction of patterns for the precipitates S1, S2 and S3, presented the HA phase - $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, according to JCPDS card 9-342. A typical example of which was shown in Fig 4-a for additional rate of $8.0 \text{ mL}\cdot\text{min}^{-1}$ (S3). The fast rate addition (S4) led the formation of an unknown phase (Fig 4-b). When the acid solution is added at a time (S4), the rate addition of reactants is higher than the rate of their consumption. Therefore the calcium and phosphate ions concentrations in solution built up during the acid addition period, making the bulk more acid and eventually the solution become supersaturated [7].

The precipitates calcined at 800°C for 3h resulted in the increase of cristallinity of the HA phase (Fig 4-II). The unknown phase at this temperature yielded β -TCP (tricalcium orthophosphate - JCPDS card 9-169) and a minimum quantity of CaO in the sample S4. The heat treatment at $1200^\circ\text{C}/3\text{h}$ for the samples increased the cristallinity of the powders and was observed that the β -TCP phase decreased in the sample S4. According to Osaka et al (1991) the unknown phase is a precursor of TCP and that too high addition rate of the phosphoric acid solution introduces a Ca-deficient precipitate [4].

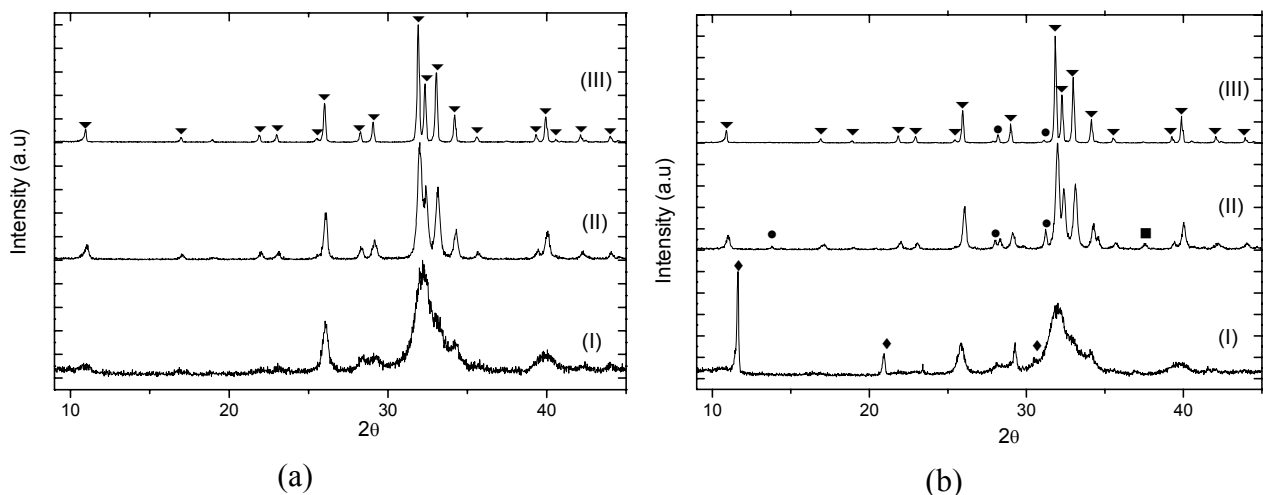


Fig 4 X-ray diffraction patterns of HA for the samples when the H_3PO_4 solution was added (a) at $8.0 \text{ mL}\cdot\text{min}^{-1}$ (S3) and (b) at a time (S4). Patterns (I) as-prepared powders, (II) after the heating treatment at $800^\circ\text{C}/3\text{h}$ and (III) after the heat treatment at $1200^\circ\text{C}/3\text{h}$. Where (▼) HA, (◆) unknown phase, (●) β -TCP and (■) CaO.

The FTIR spectra of the powders calcined at 800°C are shown in Fig 5. All samples had a similar IR profile assigned to PO_4^{3-} groups, hydroxyl (OH^-) and water (absorbed and occluded) as observed by literature [13,14].

In biological apatites, some of PO_4^{3-} ions are substituted by CO_3^{2-} ions. All the samples yields the ν_3 vibrations of C-O in the high-energy region between 1411 and 1453 cm^{-1} and ν_2 vibration in the low-energy region in 877 cm^{-1} . The peak position of the carbonate ν_2 mode depends upon whether the CO_3^{2-} ion substitutes for OH^- or PO_4^{3-} in the HA lattice [15,16]. Presence of small amounts of CO_3^{2-} ions in the stoichiometric HA powder was probably due to conducting the experiments in air [4,17].

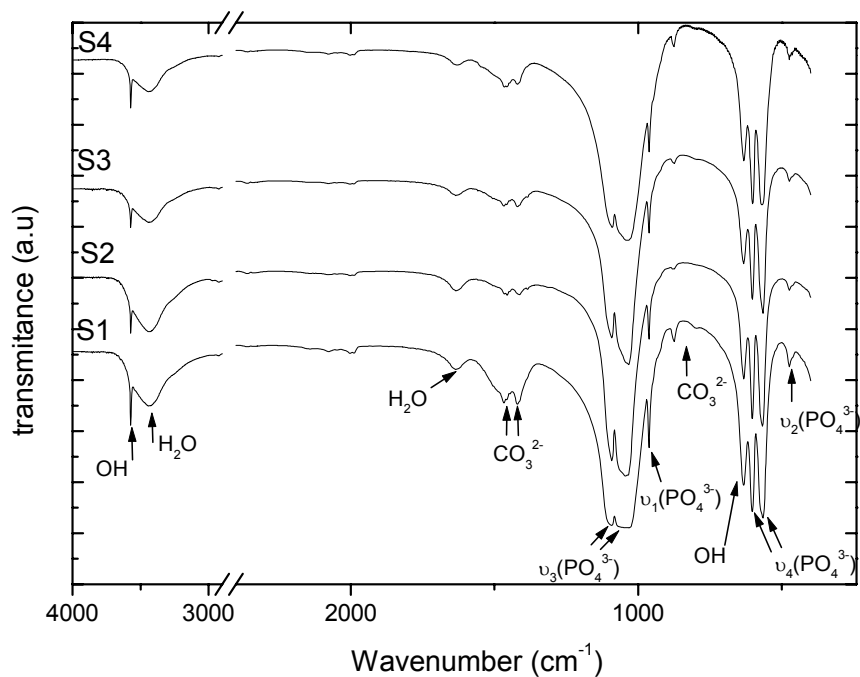


Fig 5 FTIR spectra of the powders after heat treatment at 800°C/3h. S1 = 1.0 mL.min⁻¹; S2 = 1.5 mL.min⁻¹; S3 = 8.0 mL.min⁻¹ and S4 = fast addition

Calcination at 800°C/3h leads to homogeneous powders for the samples S1, S2 and S3 with the presence of aggregates and/or agglomerates consisting of nanosized primary particles (Fig 6-a). In contrast, S4 showed different morphology that can be ascribed to HA and β -TCP phases (Fig 6-b). The BET analysis of these powders leads to decreasing to specific surface area from 34.0 m²/g for S1 to 13.0 m²/g for S4 when the addition rate of the acid in the Ca(OH)₂ suspension became faster.

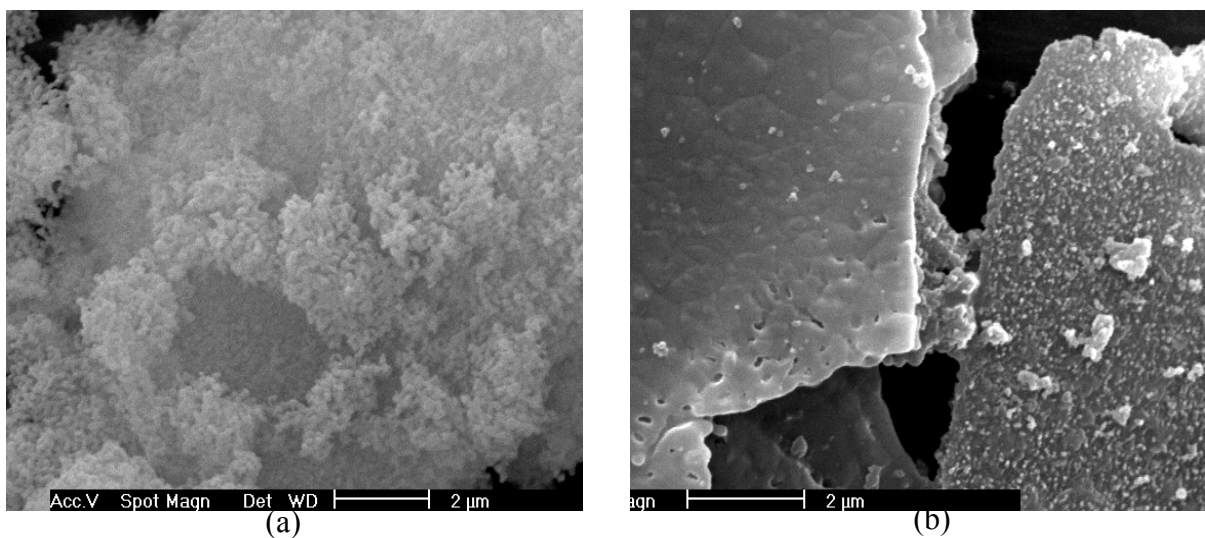


Fig 6 SEM of the samples after the heat treatment at 800°C/3h. (a) S1 = 1.5 mL.min⁻¹ and (b) S4 = fast addition.

Conclusions

The neutralization method was effective in the hydroxyapatite nanopowders obtention. All samples showed a high initial pH (>8.0) where HA is known to be stable. The ratio of addition of the acid had influence both the morphology and the formation of the phases (HA and TCP). The synthesis for HA obtention in rates up to 8.0 mL.min⁻¹ is more indicate because precipitated anions (PO₄⁻³) are generated slowly in solutions containing the metal ion (Ca²⁺). Another phase (β-TCP) was observed when the synthesis was performed at a time.

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